Microfabrics of Lacustrine Sediments to Pollutant Adsorption from a Polluted Eutrophic Lake, the Yangtze Delta Region

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ABSTRACT


Two types of microfabrics relating to pollutant adsorption were studied in the scanning electronic microscope (SEM) in a polluted, eutrophic lake, the Yangtze delta region. Agglutinational texture or the aggregates of small particles are composed of clay minerals and fine organic fragments among the silty grains and the coatings with a thickness about 1μm were present on the surfaces of the silty grains in the sediments. The chemical constituents of the aggregates and the coatings are K, Na, Ca, Mg, Si, Al, O, Fe, Ti, C, N and P determined in X-ray energy spectrometry connected with the SEM. In some cases, Pb was detected in the aggregates in the top sediment. It is suggested that nutrients and metals are adsorbed to the aggregates, which were formed by electrostatic attraction of physico-chemical floes. The coatings on the surface of quartz grains were formed by the interaction of dissociated Al, Si, Fe, etc from silicates with dissolved N, P and C nutrients in interstitial water, which was aroused by human pollution to the lake in recent two decades.

ADDITIONAL INDEX WORDS: Coatings, aggregates, pollutants.

INTRODUCTION

Adsorption and desorption of pollutants and nutrients of the sediments are important processes for water quality. Previous works were focused on the chemical adsorption of heavy metal, nutrients and pesticides (VINK and VAN DER ZEE, 1997; GAO, et al., 1998; KOELMANS, 1998; PETROVI, et al., 1998; RUAN and GILKES, 2000; KONING, et al., 2000; SAVENKO, 2001). Since the clay minerals with negative charges attract the elements with positive charges, clay minerals for adsorption of pollutants was emphasized (OLOUGHIL, et al., 2000; TARASEVICH and KLIMOVA, 2001; BRADBURY and BAEYENS, 2000). Chemical and biogenic coatings on the surfaces of grain particles of the sediments were common and can be seen in naked eyes. The reduction of Fe(III) coating in groundwater aquifers was believed for the responsibility for water quality (SAUNDERS et al., 1997; BROWN et al., 2000; KNAPP et al., 2002). These coatings were reported to absorb toxic pollutants of Cd (SCHLEKAT et al., 1998). Further laboratory studies on surface coatings by DONG et al. (2001) indicated that the adsorption of Pb to Mn oxides and the adsorption of Cd to Fe oxides were statistically higher than the adsorption of Pb and Cd to other components.

Pollution and eutrophication in lakes is a serious problem in the world. In China, many lakes have been polluted with the development of industries and agriculture since the 1980s, particularly in the middle and lower reaches of the Yangtze River. Eutrophication is one of the serious problems in the lakes, with frequent outburst of heavy cyanobacteria in the summer (CHEN and GAO, 1998; TANG and XIE, 2000; XIE and LIU, 2001). It is believed that high concentrations of nitrogen and phosphorus are the main cause for cyanobacteria bloom (PAERL et al., 2001). Previous studies have focused on chemical mechanisms of the adsorption and desorption of nutrients to bottom clay (RUTTENBERG, 1992 and 1994; SLOMPO et al., 1998; WANG et al., 2000). Chemical and biological indexes were used to evaluate or monitor lake pollution (FAN, 1995; FAN et al., 1998; YE et al., 1995). However, much less attention has been paid to the microfabrics physical forms of pollutant adsorption in bottom clay. Microfabric techniques were used in sediment studies to reveal sedimentary dynamics in marine and delta sediments (GILBERT, 1969; BENNETT, et al., 1981; KUEHL, et al., 1988; REYNOLDS and GORSLINE, 1991), lacustrine and fluvial sediments (TANG, et al., 1994; SACK and LAST, 1994), glacial till (VAN DER MEER, 1993; YI, 1997), debris flow (FANG, et al., 1991). Microfabric is a physical feature of sediments and can be used to describe the bondage and separation of sediments. Different microfabric types have different capacities against separation by wave action and dissolution, etc., which may arouse desorption. Thus, understanding microfabrics relating to pollutant adsorption is one of the basic steps to understand pollutant desorption from sediments. This paper studies two microfabrics of aggregates and coatingss relating to pollutant adsorption in modern lacustrine sediments, and discusses their origins of pollutant adsorption to the sediments in a polluted, eutrophic lake, the Yangtze delta region.

SAMPLING SITES

Taihu, the third largest freshwater lake in China, is located in the delta of the Yangtze River in eastern China (30°05’ 32° 08’N; 119°08’ 121°55’S) (Figure 1). It is a shallow lake with a surface area of 2,338 km² a catchment area of 36,500 km² and a mean depth of 1.9 m. Seven large- and medium-sized cities and 31 county towns are around the lake (SHEN et al., 2000), with about 35 million people (2.9% of the nation’s population) in the catchment. The catchment has 2.66 x 10⁶ ha farmland to which 2-3 million tons of chemical fertilizer and 70 80,000 tons of pesticides are applied annually, resulting in 1.5 million tons of chemical fertilizers and pesticides being washed into the lake each year. The lake is also the main source of water supply for Wuxi City with a population of 4.3 million and a major fishery base. Intensive fish-farming increased nutrient inputs to the lake. The water quality of Lake Taihu has worsened severely over recent decades with a change from mesotrophic in the
1950s to eutrophic now (Pu et al., 1998; QN, 1999; Qu et al., 2000). Cyanobacteria outburst in Taihu is one of the most serious problems in China since the 80s of the last century.

METHODS

Coring and Lithostratigraphy
Sediment cores were taken from four locations within western Taihu (Figure 1) in October 1998. At each location, four longer static-pressure cores (Tai1 L - Tai 4L) within 90cm were taken and a short gravity core (Tai1S). The longer cores were stored in PVC tubes and brought back to the laboratory for microfabric analysis. Analyses of geochemical elements and SCPs (small carbonished particles) on Tai1S were done.

Microfabrics and Chemical Constituents
The Tai1L, Tai2L, Tai3L and Tai4L were cut along the long axis using an electrical osmotic knife. Subsamples in one-half of the tube were selected in one centimeter interval to determine the grainsize. The out layer of the sample in other half of the tube was removed after it was immerged in acetone in three times in order to remove water. Subsamples were collected and were sprayed in gold for microfabric studies. Some subsamples were also taken out to remove the water in freeze-dry method in order to compare the results with those treated by chemical method. Microfabrics were observed in the SEM and the chemical elements in clay-sized particles and on the surface of silt grain particles were determined by X-ray energy spectrometry. Some subsamples were sprayed in carbon also for the determination of chemical elements in order to avoid the flap of the peaks of phosphorous and silicon.

Because of the material loss or disturbance at the top sediment in osmotic cutting, Tai1L, Tai2L, Tai3L and Tai4L were separated, starting at 2cm, 8cm, 5cm and 3cm for microfabric study, respectively. The subsamples in Tai1L, Tai2L, Tai3L and Tai4L were selected with one to four centimeter intervals for the SEM observation. Five samples in Tai3L were selected for the observation. One to two photos with the amplification of 1000-2000 for each sample were used for measurements. The shapes of all particles and voids in the SEM's photos were summed up into rectangle, triangle, trapezium and round. The particles measured were only silt grain and the aggregates of clay particles were not measured. The necessary linear parameters to calculate the areas of particles and voids were measured in the photos. The average size of a particle or a void was calculated by the square root of its area.

SCPs (small carbonished particles) are produced from the high temperature combustion of fossil-fuels and have no natural sources. Therefore, in lake sediments they provide an unambiguous record of industrially-derived, atmospherically deposited pollution. The procedure for extraction and enumeration of SCP from the Tai1S and Tai1L sediment cores followed Rose (1994). Sediment concentrations were calculated as 'number of SCPs per gram dry mass of sediment' or gDM⁻¹.

Nitrogen and phosphorus analysis was undertaken on the Tai1S core. Sediment nitrogen analysis followed an adapted
Kjeldahl digestion followed by a distillation procedure (Allen, 1989) whilst sediment phosphorus analysis employed a perchloric-sulphuric acid digest followed by a colorimetric measurement (Allen, 1989).

RESULTS

Microfabrics

Three types of microfabrics relating to pollutant adsorption are agglutinational texture, coatings and microvoids. Agglutinational texture is the aggregates of clay minerals with fine organic-matter fragments. Aggregates were usually among the silt particles or clay particles and fine organic fragments assembled together solely (Figures 2A and 2B).

The difference of agglutinational texture between Taihu Lake and the lakes in the middle reach of the Yangtze River is that the presence of the framework of silty grains. The aggregates of clay particles are present among the silty particles in Taihu lake; whilst there were no framework of silty particles enclosing the aggregates of clay particles in the latter (Yi et al., 2002). Analytical results of more than ten samples by X-ray energy spectrometry showed that geochemical constituents of the integrates were K, Na, Ca, Mg, Si, Al, O, Fe, Ti, C, N and P (Figure 3A). In some cases, Pb was detected in the top sediment.

Coating is on the surface of silty grains (Figure 2C and 2D). In the bombing of the electronic beam when determining the elements of the coating, a coating was retroflexed, with a thickness of less than 1μm (Figure 2D). The geochemical elements determined by X-ray energy spectrometry are K, Na, Ca, Mg, Si, Al, Fe, Ti, C, N, P (Figure 3B and 3C). The coating and aggregates are present from top to bottom of the sediments.

The appearance and geochemical components were not found to change significantly with the depth, based on more than ten samples in each of Tai1L, Tai2L and Tai4L.

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The sediment N and P profiles of Tai1S (Figure 5) show agreement with the known eutrophication and decreasing water quality of Taihu over a period of decades. P concentrations increase steadily from the base of the core to the present and this may be interpreted as a record of aqueous P. N levels increase dramatically from the mid-1980s and this is in agreement with N concentrations in lake water which have been reported to have increased from 1.84 mg L⁻¹ in 1987 to 2.5 mg L⁻¹ in 1994.

Figure 3. Spectrometry of the chemical elements of the aggregates (A) and coatings (B, sample sprayed with gold and C, sample sprayed with carbon).

Figure 4. The changes of the sizes of particles and voids with the depth. Tai1L (Down), Tai2L (middle) and Tai4L (upper). VS void size; PS particle size.

Figure 5. The changes of the sizes of particles and voids with the depth. Tai1L (Down), Tai2L (middle) and Tai4L (upper). VS void size; PS particle size.
The SCP profile for Tai1S (Figure 6) shows low concentrations up to 30 cm (c. 1930s) followed by a massive increase in concentration in the 1940s and 1950s. Above this concentration change flattens with a peak of 9000 gDM\(^{-1}\) at 6-7 cm (c. 1990) followed by a decline to the sediment surface. Conversion of SCP concentrations to accumulation rates (no. cm\(^{-2}\) yr\(^{-1}\)) shows similar trends, although the increase in sediment accumulation rate towards the top of the core alters the ‘flattened’ section to a trend of more continuous increase. SCP accumulation rate peaks at c. 1991 at 4000 cm\(^{-2}\) yr\(^{-1}\) whilst surface levels are lower at 2400 cm\(^{-2}\) yr\(^{-1}\). These values are equivalent to levels observed in some of the more contaminated lakes in Europe.

SCP profile features are thus in broad agreement with SCP profiles from other areas of the world (e.g. Europe) where a rapid increase in concentration is observed at a similar time whilst a concentration peak is observed slightly earlier (late 1970s) (Rose et al., 1999).

**DISCUSSIONS**

**Pollutants in Aggregates**

Previous works on adsorption of pollutants were studied in chemical analyses (Vink and Van Der Zee, 1997; Gao et al., 1998; Koelmans, 1998; Petrovi, et al., 1999; Ruan and Gilkes, 2000; Koning, et al., 2000; Savenko, 2001). Clay minerals with negative charges were reported to attract the elements with positive charges and pollutants (OLoughlin et al., 2000; Tarasevich and Klímova, 2001; Bradbury and Baeyens, 2000). Clay minerals and fine organic fragments have large specific surface area and their capacity of adsorption to metal ions is high. That is why the metal elements were detected in the aggregates (Figure 3A). The pH value of the lake water is moderately alkaline in Taihu. Most of phosphorus, nitrogen, carbon and toxic elements discharged into the lake through river transportation are in dissolved status or in suspension. They are usually charged and can be adsorbed by clay minerals or organic fragments. The aggregates contain organic fragments from plants, but the phosphorous content is lower than 1% in plants fragments. When the concentration is lower than 1%, it is difficult to detect the presence of this light element in X-ray energy spectrometry. The phosphorus is detected to be present in the aggregates, indicating that the pollutants were adsorbed to the aggregates.

**Pollutants in Coatings**

Chemical and biogenic coatings on the surfaces of grain particles of the sediments which were referred to in most literatures can be seen directly in naked eyes (Saunders et al., 1997; Brown et al., 2000; Knapp et al., 2002; Schlekat et al., 1998; Dong et al., 2001; Penn et al., 2001). The origin of the coatings of iron oxides and magnesium was largely ascribed to action of bacteria and diatoms (Boult et al., 1997; Davaud and Girardclos, 2001; Allouc and Harmelin, 2001). The compositions of nutrient elements in the coatings suggest that they may be ascribed to the biofilms.

However, the appearance of the coating -- very smooth surface and small thickess, in Taihu sediment is similar to gelatinous texture in blue clay with about 40% of clay fraction with the size less than 1 \(\mu\)m and with higher organic content of 2.9-8.0%, but not common in black gray with large amount of coarse organic fragments in Honghu, a clean lake (Yi, 2001). It is also not present in gray clay with low organic matter content in the sediments of clean lakes and the swamp sediments with high content of coarse organic matter in a orographic basin, the middle reach of the Yangtze River (Yi, 2001; Yi et al., 2002).

The coatings have the similar chemical compositions with those of gelatinous texture. The appearance and chemical compositions suggest that the coating may have the same genesis as that of gelatinous texture. The phosphorus content is lower than 1% in bacteria and diatoms. If the content of phosphorus is lower than 1%, it is difficult to detect the presence of this light element in X-ray energy spectrometry. The phosphorus is detected to be present in the coatings, suggesting that the coatings were not only the microbio, but contain pollutants.

Based on the comprehensive studies on the water of Taihu during 1950-1995, the water quality and nutrient conditions increased one level in every 10 to 15 years, and TN and TP increased by 66% and 79%, respectively from 1987 to 1995 (Fan, 1996). Percentage of retention of TN and TP (ratio of the net amount of TN or TP discharged into the lake to the amount of TN or TP in situ) were 1.33 and 6.8, respectively during 1987-1988 (Jin et al., 1995). It is believed that the gelatinous texture is formed by combining dissociated oxide of Fe, Al, Si with organic gelatin and then formed into a gelatinous shape (Wang, et al., 1988). It is suggested that the coatings on the surface of the sediment grains were formed by the interaction of the Nutrients of nitrogen, carbon and phosphorous, etc. from pollutants with the dissociative Fe, Al, Si from silicate minerals.

Figure 5. Sediment profiles of total nitrogen (%) and total phosphorus in Tai1S.

(SUN and HUANG, 1993). High N/C ratios are generally associated with algae and hence the dramatic increase in sediment N may reflect the increased severity of algal blooms in the lake in recent years.

Figure 6. Sediment profiles of SCP concentration (gDM\(^{-1}\)) in Tai1S.
Based on the sedimentary datings of Tai1S and Tai4S in 210Pb and 137Cs (YI et al., 2003 in press), the coatings were still present in the sediment formed before the 1980s of serious pollution period. As compared with gelatinous texture in the sediments from clean lake water mentioned above, the coatings might be formed in a natural process in Taihu. SCP accumulation rate peaks in c. 1995 at 4000 cm² yr⁻¹ (Figure 6), being close to the beginning of serious pollution period in Taihu. The TN and TP in sediments decreased with the depth in Tai1S (Figure 5). FAN et al. (2000) also showed the same results in Taihu. But they studied the vertical changes of the concentrations of nitrogen and phosphorus in interstitial water in the sediment of 30cm thick and found that their concentrations tended to be increasing with the depth and besides, were not related with the TN and TP, respectively. The void sizes in Tai1L and Tai4L display a slight decrease with the depth (Figure 4), implying the exchange of chemical elements in interstitial water may not be affected by void sizes. Below a certain depth, the interstitial water will be closed without exchanging with the upper water and the nutrient elements of C, N and P and other geochemical elements in interstitial water may precipitate on the surfaces of quartz grains, forming the coating.

CONCLUSIONS

To understand adsorption of pollutants to and desorption from sediments, the use of microfabric techniques is helpful to identify the presence of pollutants in the sediments. The microfabric forms of aggregates and coatings relating to pollutant adsorption were found in lacustrine sediment in Taihu lake, the Yangtze delta region. The aggregates or agglutinational texture is composed of clay minerals and fine organic fragments which adsorb the pollutants among silty grains. The coatings are on the surface of quartz silty grains. The appearance and chemical components suggest that they are a chemical compound and may be precipitated by pollutants in interstitial water aroused by human activities.

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LITERATURES CITED


